

N. Qureshi · S. Hughes · I. S. Maddox · M. A. Cotta

Energy-efficient recovery of butanol from model solutions and fermentation broth by adsorption

Received: 30 November 2004 / Accepted: 18 January 2005 / Published online: 3 March 2005
© Springer-Verlag 2005

Abstract This article discusses the separation of butanol from aqueous solutions and/or fermentation broth by adsorption. Butanol fermentation is also known as acetone butanol ethanol (ABE) or solvent fermentation. Adsorbents such as silicalite, resins (XAD-2, XAD-4, XAD-7, XAD-8, XAD-16), bone charcoal, activated charcoal, bonopore, and polyvinylpyridine have been studied. Use of silicalite appears to be the more attractive as it can be used to concentrate butanol from dilute solutions (5 to 790–810 g L⁻¹) and results in complete desorption of butanol (or ABE). In addition, silicalite can be regenerated by heat treatment. The energy requirement for butanol recovery by adsorption–desorption processes has been calculated to be 1,948 kcal kg⁻¹ butanol as compared to 5,789 kcal kg⁻¹ butanol by steam stripping distillation. Other techniques such as gas stripping and pervaporation require 5,220 and 3,295 kcal kg⁻¹ butanol, respectively.

Keywords Butanol · Adsorption · Silicalite · ABE · Recovery · Polyvinylpyridine

Mention of trade names of commercial products in this article/publication is solely for the purpose of providing scientific information and does not imply recommendation or endorsement by the United States Department of Agriculture.

N. Qureshi (✉) · M. A. Cotta
United States Department of Agriculture,
National Center for Agricultural Utilization Research
(USDA, NCAUR), Fermentation Biotechnology,
1815 N University Street, Peoria, IL 61604, USA
E-mail: qureshin@ncaur.usda.gov
Tel.: +1309-681-6318
Fax: +1309-681-6427

S. Hughes
USDA, NCAUR, Bioproducts and Biocatalysis,
1815 N University Street, Peoria, IL 61604, USA

I. S. Maddox
Institute of Engineering and Technology,
Massey University, Palmerston North, New Zealand

Introduction

Butanol is an important feedstock chemical and fuel that can be produced by fermentation using renewable resources as substrates [1–2]. This fermentation (also called acetone butanol ethanol (ABE) or solvent fermentation) was important during the early part of the last century and ranked second to ethanol [3]. Unfortunately, fermentation plants were forced to cease operation owing to the development of the petrochemical industry. The sole butanol fermentation plant that was operational until the early 1980s was closed owing to the increased cost of substrate (molasses) caused by severe drought. Before the 1980s this fermentation faced numerous problems that kept it from remaining a commercially viable process. Research interests in this type of fermentation have revived, however, as a result of fluctuating oil prices and depletion of fossil fuels. The microbial cultures that are capable of producing significant amounts of butanol include *Clostridium acetobutylicum* or *C. beijerinckii*.

One of the most significant challenges faced by commercial butanol fermentation was the prohibitive cost of the recovery of butanol from broth, due to its low concentration (<20 g L⁻¹) and higher boiling point than water [1, 4]. At such a low concentration of solvents, the energy required for butanol separation by traditional distillation is higher than the energy content of the product itself [5]. In addition, as the final concentration of butanol reaches 20 g L⁻¹ in the fermentation broth, the culture stops further fermentation. Due to the toxicity of butanol, concentrated sugar solutions that further complicate disposal of large waste streams cannot be used, thus worsening the process economics. In traditional batch fermentation, sugar solution of concentration higher than 60 g L⁻¹ cannot be used.

In order to remove butanol in a more energy-efficient way; during fermentation, a number of product removal techniques have been investigated [1, 6–8]. The techniques that have been applied to ABE fermentation

include adsorption, gas stripping, liquid–liquid extraction, pervaporation, perstraction, and reverse osmosis. These techniques have been applied for the purpose of removing butanol during fermentation in order to reduce butanol inhibition. During the application of most of these techniques, improved reactor productivities and higher sugar utilization have been obtained as a result of reduction in product inhibition, thus making the butanol fermentation process more energy-efficient [3, 6–7].

Among the above product removal techniques, gas-stripping, liquid–liquid extraction, and pervaporation have been favorably viewed as butanol recovery techniques to be applied at a commercial level [8]. In recent studies, adsorption has been identified as a simple technique that can be applied successfully for energy-efficient removal of butanol from fermentation broth [9–10]. These studies have demonstrated that adsorption requires less energy for butanol separation than any other technique [10]. In addition, a concentrated butanol stream is obtained. As a result of identification of adsorption as a superior technique (due to rapid adsorption, ease of desorption, and regeneration of adsorbents), it is our objective to review the literature on the use of various adsorbents for butanol separation and concentration and present these studies and our results on energy requirements for butanol separation in a more meaningful manner.

Methods and calculations

Three different types of adsorption processes have been used including batch, continuous column, and continuous column with cell separation using ultrafiltration or microfiltration membranes (Fig. 1). A schematic diagram of the separation and concentration of butanol from fermentation broth using silicalite is shown in Fig. 2. Before developing this process, material and energy balance equations were developed for butanol adsorption [10]. Presenting material and energy balance equations is beyond the scope of this article, however, a comparison of energy requirements for various techniques has been made. The adsorption capacities in a batch adsorption process were calculated using the following equation $[(C_{ba}-C_{aa}) \times V_F] \times W_a^{-1}$, where C_{ba} , C_{aa} , V_F , and W_a are butanol/ABE concentration before adsorption (g L^{-1}), butanol/ABE concentration after adsorption (g L^{-1}), volume of liquid feed (L), and weight of adsorbent (g) used to adsorb butanol/ABE, respectively. In situations where an adsorption column was used, V_F was taken as the liquid volume that passed through the column. In order to present the amount of adsorbent used per solution volume in a uniform manner (for a batch process), the amount of adsorbent (g) was divided by the solution volume (V_F). Although, a butanol concentration of 980 g L^{-1} has been reported to be achieved [11], the reader is advised that a butanol concentration of more than 810 g L^{-1} cannot be

obtained (specific gravity, $\rho = 0.81$). Hence, in this report it is assumed that the actual concentration that had been obtained by the authors was in the range $790\text{--}810 \text{ g L}^{-1}$.

Removal of butanol by adsorption

Model solutions

An early report of the recovery of butanol from model solutions (butanol or ABE in water) was that of Milestone and Bibby [11]. These authors used silicalite to adsorb butanol from a solution mixture containing 21.5 g L^{-1} each of butanol and ethanol. Silicalite adsorbed butanol selectively. The capacity of silicalite for butanol adsorption was found to be 97 mg g^{-1} (Table 1). In another study, a mixture containing 19.9 g L^{-1} of acetone and 20.0 g L^{-1} of butanol was used. The silicalite adsorbed 26 mg g^{-1} acetone and 90 mg g^{-1} of butanol, suggesting that both of these

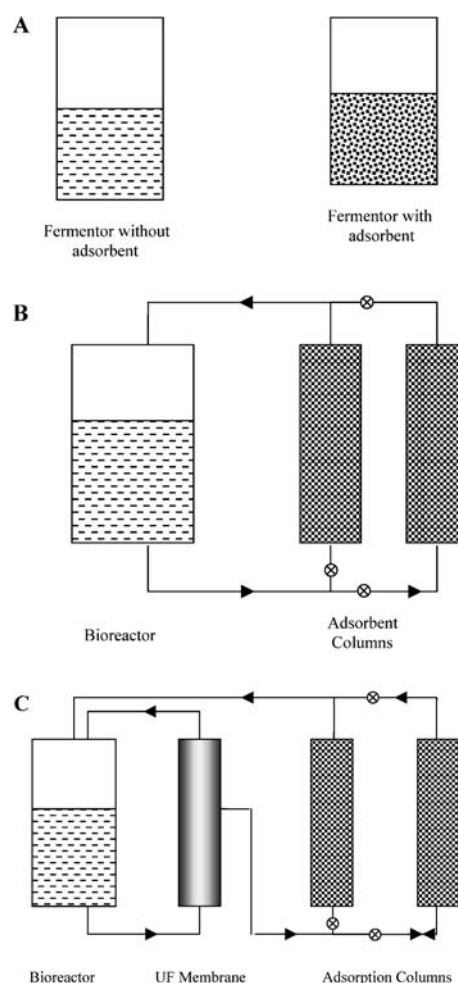
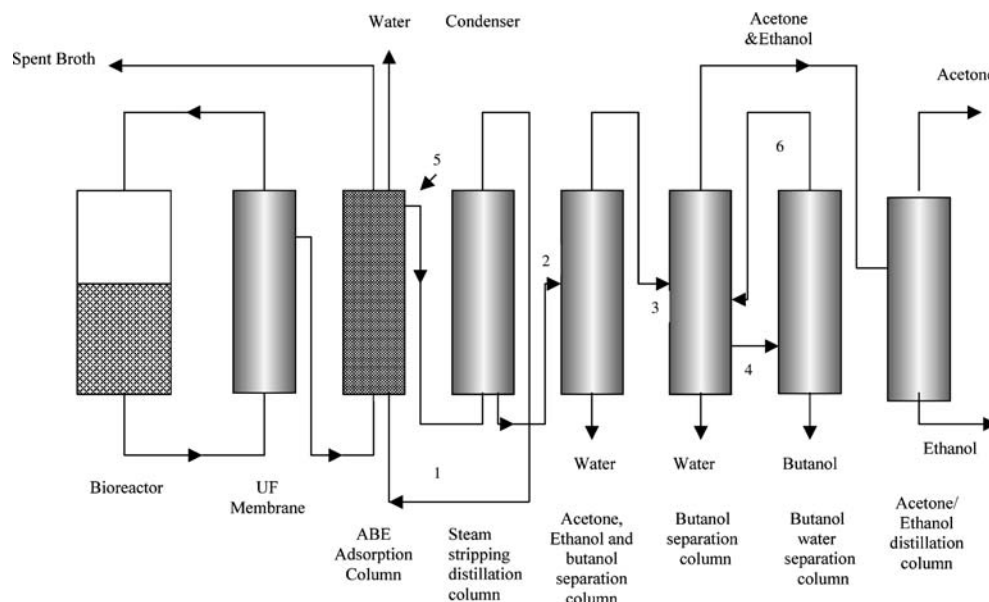


Fig. 1 A schematic diagram of butanol or ABE removal by adsorption. **a** Adsorption batch process without adsorbent and with adsorbent, **b** Adsorption using packed columns of adsorbent, **c** Cell removal by membrane prior to adsorption using packed columns of adsorbent

Fig. 2 A schematic diagram of ABE separation and concentration from fermentation broth using adsorbent. 1 Hot air to remove water or ABE from silicalite column, 2 ABE and water stream, 3 ABE water stream, 4 Butanol water stream, 5 ABE water stream, 6 Butanol water stream



products can be removed from an acetone butanol (AB) fermentation broth (Table 1) [11]. Acetone is a by-product of the butanol fermentation process with a usual concentration approximately one-third that of butanol. Following adsorption, water (adsorbed) and butanol were separately desorbed by sequential heat treatment to give a concentrated butanol solution (actual—790–810 g L⁻¹; reported—980 g L⁻¹) as a final

product. This suggested that butanol can be recovered selectively from dilute solutions using adsorption–desorption processes and silicalite. The silicalite was regenerated by heating to 200°C. It has been reported that, on heating, structural damage to silicalite does not occur below 1,000°C.

Subsequently, Das et al. [12] studied adsorption of butanol from model solutions onto various charcoals.

Table 1 Use of various adsorbents to recover butanol or ABE from model solutions

Reference	Adsorbent	Components present in feed*	Reactor Type, size [mL]	Butanol concentration in reactor [g L ⁻¹]	Adsorption temp. [°C]	Butanol adsorption capacity [mg g ⁻¹]	Amount adsorbent used [g L ⁻¹ solution]	Comments
11	Silicalite	BE	Batch, 50	21.5	20	97	40	B adsorption 90 mgg ⁻¹
12	Activated Charcoal (granular)	Butanol	Batch, 5	5.0–30.0	-	130	100	
	Bone Charcoal	Butanol	Batch, 5	5.0–30.0	-	206	100	B-C treated with 1 N HNO ₃
13	Silicalite	ABEHaHb	Batch, 5	10.0	25 ^b	48	200	Synthesized silicalite
14	Active Carbon ^a	Butanol	Batch, 100	15.0	-	252	10	Butanol solution used above
	XAD-4	Butanol	Batch, 100	14.4	-	100	10	above
	XAD-2	Butanol	Batch, 100	16.5	-	78	10	above
	XAD-8	Butanol	Batch, 100	15.5	-	66	10	above
16	Amberlite XAD-7	Butanol	Batch, 5	20.0	25 ^b	69	200	Adsorption was rapid
	Amberlite XAD-4	Butanol	Batch, 5	20.0	25 ^b	83	200	above
	Bonopore	Butanol	Batch, 5	20.0	25 ^b	74	200	above
	Bonopore – nitrated	Butanol	Batch, 5	20.0	25 ^b	55	200	above
17	Polyvinylpyridine	Butanol	Batch, 100	14.9	-	68	100	Adsorption was rapid

a – Norit-ROW 0.8

BE – butanol ethanol mixture, ABEHaHb – acetone butanol ethanol acetic acid and butyric acid mixture, B-C – bone charcoal

b – Room temperature (assumed to be 25°C)

- Not reported

Although some values were reported in wt% in literature, for simplicity we have reported them in g L⁻¹.

* Feed solution pH not reported

The concentration of butanol in the feed was 5.0–30.0 g L⁻¹. The activated charcoal adsorbed butanol at a rate of 130 mg g⁻¹ while bone charcoal adsorbed butanol at 206 mg g⁻¹ (Table 1). The adsorption capacity of bone charcoal for butanol (206 mg g⁻¹), is much greater than that for silicalite, which adsorbed 85–97 mg g⁻¹ [11]. In kinetic experiments, bone charcoal had the higher absorption capacity but with incomplete recovery on desorption. IRC-50 (nitric acid treated) and XAD-2 absorbed half as much as the charcoal with <90% recovery. Problems such as interactions between adsorbents and nutrients, sugars, biomass, toxicity of adsorbents, and the ease of desorption still remain to be addressed [12].

Further, Meagher et al. [13] synthesized silicalite and characterized it for butanol adsorption from an aqueous solution containing ABE and acetic and butyric acids. The butanol adsorption capacity for silicalite was calculated to be 48 mg g⁻¹ while its capacity for adsorbing acetone was 11 mg g⁻¹. It was reported that all the five components present in the feed were adsorbed. The adsorption of acetic and butyric acids was found to be less than 1 mg g⁻¹. Silicalite was used repeatedly for adsorption and desorption of ABE. The ABE adsorption capacity was found not to be affected by repeated use.

In order to study adsorption of butanol, Groot and Luyben [14] used active carbon [Norit W52 (powder), and Norit ROW 0.8 (extruded cylinders of 1-mm diameter and 3-mm length)] and polymeric resins (XAD-2, XAD-4, and XAD-8). The studies were performed to test the capacity for butanol (model solution) and butanol/isopropanol (fermentation) adsorption. It was discovered that active carbon (Norit ROW 0.8) adsorbed the maximum amount of butanol from a model

solution to a capacity of 252 mg g⁻¹. The adsorption capacities of resins [XAD-4 (100 mg g⁻¹), XAD-2 (78 mg g⁻¹), and XAD-8 (66 mg g⁻¹)] were lower than that of the active carbon (Table 1). No attempts were made to desorb and recover the adsorbed butanol.

Following those investigations, Nielson et al. [15–16] studied adsorption of butanol onto polymeric resins. The polymeric resins studied were Amberlite XAD-7, Amberlite XAD-4, Bonopore, and nitrated Bonopore. The adsorption capacities of these adsorbents were 69, 83, 74, and 55 mg g⁻¹, respectively (Table 1). These studies were extended for adsorption of acetone and butanol from actual fermentation broths, which will be discussed in section under fermentation broth.

Further studies on adsorption of butanol were performed by Yang et al. [17] using polyvinylpyridine as an adsorbent (Table 1). The adsorption capacity of this adsorbent was found to be 68 mg g⁻¹. It has been reported that adsorption onto the adsorbent was quick. Desorption of butanol from the resin was carried out using methanol.

From Table 1 it is obvious that adsorption capacities of activate carbon and bone charcoal were high, at 252 and 206 mg g⁻¹, respectively [12, 14]. The adsorption capacity of activate charcoal was reported to be 130 mg g⁻¹. The maximum adsorption capacity of silicalite was reported to be 97 mg g⁻¹ (Table 1). XAD-4 and Amberlite XAD-4 adsorbed 100 and 83 mg g⁻¹, respectively. Successful recovery of butanol from activated carbon would reduce adsorbent use by a factor of 2.5 as compared to Amberlite XAD-4. It is also anticipated that activated carbons can be used repeatedly; however, this will depend upon recovery of the adsorbents and their successful regeneration, which still needs to be determined.

Table 2 Adsorption of butanol onto various adsorbents to recover solvents from fermentation broth

Reference	Adsorbent	Reactor type, Size [mL]	Butanol/ABE conc. in reactor [g L ⁻¹]	Adsorption temp. [°C]	Adsorption pH	Adsorption capacity [mg g ⁻¹]	Amount adsorbent used [g L ⁻¹ solution]	Comments
18	Silicalite	batch, 10	11.7–16.8	–	–	64–85	168	Treated without removing cells
19	Adsorbent resin XAD-16	batch, 1000	9.2 ^C	4	4.96	75	85	Treated without removing cells
	Silicalite	batch, 1000	8.3	4	5.01	63.5	85	Treated without removing cells
15	Bonopore-7	e	–	–	–	90	–	Medium comp. not adsorbed
16	Amberlite XAD-7	batch, 10	4.0	–	–	22	100	pH was raised to avoid adsorption of acids
	Amberlite XAD-4	batch, 10	4.0	–	–	27	100	
	Bonopore	batch, 10	4.0	–	–	23	100	
	Bonopore nitrated	batch, 10	4.0	–	–	13	100	
17, 20	Polyvinylpyridine	batch, 100	11.2	–	–	–	100	Fermentation broth used

C – sugar not adsorbed
e - data not available

- Not reported
Butanol, ABE concentration reported in g L⁻¹ for convenience

Table 3 Removal of butanol or ABE from fermentation broth: A comparison of different parameters

Reference	Control Fermentation Parameters				Fermentation Parameters with Adsorption					
	Productivity [g L ⁻¹ h ⁻¹]	ABE Yield [g g ⁻¹]	Total ABE Produced [g]	Total sugar used [g]	Adsorbent	Process	Productivity [g L ⁻¹ h ⁻¹]	ABE Yield [g g ⁻¹]	Total ABE Produced [g]	Total sugar used [g]
20	0.40	0.31	13.5	43.8	Polyvinyl- pyridine	Batch	0.92	0.32	23.2	73.3
above	above	above	above	above		Fed-batch ^a	1.33	0.32	59.8	190.0
above	above	above	above	above		Fed-batch ^b	1.69	0.32	387.3	1198.5

a – one fed-batch cycle

b-repeated fed-batch cycles

Fermentation broth

Adsorption of acetone and butanol from model solutions has been demonstrated successfully with the objective of applying these adsorbents to actual fermentation broths. Fermentations are usually complex in nature and contain sugars, cells, nutrients, final products, and reaction intermediates. For a process to be successful, sugars, reaction intermediates, and nutrients should not be adsorbed. While adsorption of sugars has not been reported, nutrients and reaction intermediates can be adsorbed onto some adsorbents, which will be discussed later. The studies that have been conducted on using various adsorbents to adsorb butanol from fermentation broth are presented in Table 2. Interestingly, none of the adsorbents have been found to be toxic to the cultures.

Following the report of adsorption and successful recovery of butanol using silicalite [11], Maddox [18] was the first to demonstrate this process with an actual fermentation broth. The concentration of butanol before adsorption in the fermentation broth was 11.7–16.8 g L⁻¹ (Table 2). It was demonstrated that 41–96% of the butanol available in the fermentation broth was adsorbed with adsorption capacities ranging from 64 mg g⁻¹ to 85 mg g⁻¹.

In another study, ABE was adsorbed from the effluent of an immobilized cell reactor onto the adsorbent resin XAD-16 and silicalite [19]. The object of this exercise was to remove butanol, which is toxic to the cells of *Clostridium acetobutylicum*, and to recycle the treated effluent to the reactor for utilization of the residual sugar. The ABE adsorption capacities of silicalite and XAD-16 resin were 84 and 90 mg g⁻¹, respectively (Table 2). The butanol adsorption capacities of the two adsorbents were 63.5 and 75 mg g⁻¹, respectively. Both of the adsorbents removed acetone and butanol. Lactose was not removed from the broth using these adsorbents.

Nielsen et al. [15, 16] tested a number of adsorbents and found bonopore 7 (a copolymer of divinylbenzene/styrene) to be a suitable adsorbent. It adsorbed butanol at the rate of 90 mg g⁻¹ of polymer. The feasibility of the process was tested in an integrated system. These authors also tested Amberlite XAD-7 and Amberlite XAD-4 with the fermentation broth and

reported butanol adsorption capacities of 22 and 27 mg g⁻¹, respectively (Table 2). Repeated batch cultures from which the cells were removed by centrifugation before treatment with bonopore gave good butanol production and increased substrate utilization compared to untreated cultures. Cell recycling rather than a whole broth led to greater butanol recovery, presumably because in the latter process bacterial cells adhered to the adsorbent, thus fouling it. Adsorbents exerted a significant effect on the overall fermentation by decreasing the level of butanol below the toxic level.

Yang et al. [17] used polyvinylpyridine to adsorb butanol from fermentation broth. Adsorption kinetics of butanol and butyric acid from the fermentation broth showed that both of the components were adsorbed onto this resin. The concentration of butanol in the eluted phase was increased by a factor of 3–4. Also, inhibition from acids was reduced during the first phase, since they were adsorbed by the resin. As acid concentration decreased, more butanol was adsorbed and the cells suffered less inhibition during the second phase.

Process integration

One of the advantages of novel product recovery techniques is to improve reactor productivity and sugar utilization by integrating fermentation and recovery [1, 5–6]. Yang and Tsao [17, 20] used this approach to produce butanol and simultaneously remove it by adsorption onto polyvinylpyridine resin. In control batch fermentation, reactor productivity and sugar utilization of 0.40 g L⁻¹ h⁻¹ and 43.8 g, were obtained, as compared to 0.92 g L⁻¹ h⁻¹ and 73.3 g, respectively, in a similar reactor with product recovery by adsorption (Table 3). The productivity and sugar utilization were further improved to 1.33 g L⁻¹ h⁻¹ and 190 g in a one-cycle fed-batch system. Furthermore, a repeated-cycle fed-batch reactor resulted in a productivity of 1.69 g L⁻¹ h⁻¹ and sugar utilization of 1198.5 g. In the four systems (control, batch product recovery, one-cycle fed-batch product recovery, and repeated-cycle fed-batch with product recovery) total solvent production of 13.5, 23.2, 59.8, and 387.3 g

were achieved, respectively. The application of product recovery by adsorption has demonstrated that significant improvements can be achieved in terms of improved ABE production, high productivity, and high sugar utilization, in addition to energy-efficient product recovery.

Butanol recovery by desorption

Among the various adsorbents studied, three have been used to recover butanol, including silicalite, charcoal, and polyvinylpyridine (Table 4). Using silicalite as an adsorbent, butanol concentration as high as 790–810 g L⁻¹ (reported—980 g L⁻¹) has been achieved in the final product from a feed solution containing 5 g L⁻¹ butanol [11]. The adsorbed water was removed from silicalite by heating to 40°C, while butanol was removed by heating to 150°C. Sequential heating of the silicalite helped to obtain a concentrated butanol solution (790–810 g L⁻¹). Such a sequential heating process would result in the consumption of less energy thus making butanol recovery by adsorption/desorption more energy-efficient.

Meagher et al. [13] also desorbed butanol and other components (acetone and ethanol) by heat treatment of silicalite to 78°C. The recovery of butanol, acetone, and ethanol was 100, 95.5, and 80.0%, respectively, of the adsorbed amounts. No attempts were made, however, to estimate concentration of ABE in the desorbed phase. These studies suggested that desorption of ABE is possible at temperatures lower than 150°C thus saving more energy during the recovery process.

Yang et al. [17] desorbed butanol (including acetone, ethanol, acetic acid, and butyric acid) from polyvinylpyridine resin, using methanol as a displacer. Methanol was chosen because of its low boiling point. All the adsorbed components were desorbed in two bed volumes of methanol. The desorption process was rapid, indicating an easy reversibility of the equilibrium. It has been reported that good reversibility is important in the industrial processes for butanol recovery and reuse of adsorbent [17]. The concentration of butanol in the eluant was increased by a factor of 3 to 4.

Attempts were also made to desorb butanol from bone charcoal by passing hot air at 120°C through the charcoal column/bed [12]. The exit air was cooled to 0°C

in order to condense butanol. The recovery of butanol was 60–65% of that adsorbed. Experiments were also conducted to recover adsorbed butanol from IRC-50 (nitrated) and XAD-2, however, only 75–85% butanol was recovered.

Energy requirement

In an effort to compare the energy requirement for butanol separation using various recovery processes, a butanol adsorption—desorption and concentration process was developed (Fig. 2). The material and energy balance suggested that recovery of butanol from fermentation broth using silicalite would require 1,948 kcal kg⁻¹ recovered butanol (Fig. 3). These calculations assume that the silicalite column adsorbs 50% water which can be desorbed at 40°C [11, 21] to achieve a butanol concentration of 810 g L⁻¹. Butanol recovery by steam stripping and distillation requires 5,789 kcal kg⁻¹ butanol followed by gas stripping (5,220 kcal kg⁻¹ butanol), pervaporation (3,295 kcal kg⁻¹ butanol), and liquid–liquid extraction (2,119 kcal kg⁻¹ butanol) [9].

Adsorption of cells, nutrients, and reaction intermediates

Direct use of adsorbents without removing cells from the fermentation broth may foul the adsorbents. In order to overcome this problem, either a microfiltration or an ultrafiltration membrane can be placed between the adsorption column and bioreactor or cells can be centrifuged and returned to the reactor. The first approach was applied by Yang and Tsao (Fig. 1c) to improve adsorption efficiency and avoid fouling of adsorbent [20]. In addition to achieving greater product adsorption, high reactor productivities were also achieved due to increased cell concentration in the reactor, thus making the overall process of butanol production from renewable resources more energy efficient. The permeate of the microfiltration/ultrafiltration membrane was treated for ABE removal. The second approach was investigated by Nielson et al. [16]. In this process, cells were centrifuged before treating the clear fermentation broth with adsorbents.

Another problem with the use of adsorbents is removal of nutrients during the treatment process [16–17,

Table 4 Recovery of butanol/ABE using adsorbents

Reference	Adsorbent	Butanol concentration in feed [g L ⁻¹]	Butanol concentration in recovered product [g L ⁻¹]	Comments
11	Silicalite	5.0	790–810*	Water was removed by heating silicalite to 40°C
12	Activated charcoal	5.0–30.0	—	Only 60–85% of the sorbed alcohol recovered
17	Polyvinylpyridine	10.0	30–40	Recovered in methanol phase
21	Silicalite	10.0	500	

-Not reported * Reported value
980 g L⁻¹

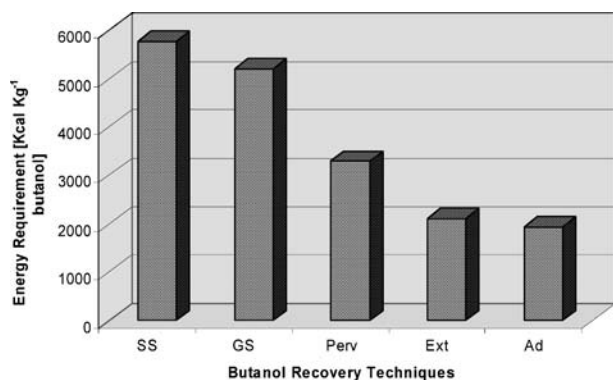


Fig. 3 A comparison of energy requirement to separate ABE from fermentation broth using various energy-efficient techniques. SS—steam stripping distillation; GS—gas stripping; Perv—pervaporation; Ext—liquid–liquid extraction; Ad—adsorption on to silicalite

[19]. Adsorption of nutrients would reduce further fermentability unless additional nutrients are added. Addition of nutrients would add to the cost of fermentation. Nielson et al. [16] reported that use of bone charcoal neither removed essential medium components nor left any negative effect on cell growth; however, when the fermentation broth was treated with XAD-4, it drastically reduced the fermentability of the medium. The effect of XAD-4 was overcome by adding additional yeast extract, suggesting that some vital nutrients were adsorbed to the resin. Ennis et al. [19] also reported adsorption of nutrients by XAD-16. Adsorption of nutrients can be alleviated by using a minimal medium to support growth and fermentation before treatment, thus leaving behind no nutrients to be removed. In such cases further fermentation can be conducted by recycling the treated broth supplemented with nutrients.

Butanol fermentation is associated with the production of reaction intermediates during the acidogenic phase, including acetic and butyric acids. Adsorption of these acids onto the adsorbents should be avoided, as these are required to achieve high butanol or ABE yields. Further, their adsorption may cause additional problems during concentration and purification. Adsorption of acids has been reported by Ennis et al. [19] (acetic acid), Yang et al. [17], Meagher et al. [13] (butyric acid on repeated use; 4 mg g⁻¹ silicalite), and Nielson et al. [16]. In order to avoid adsorption of butyric acid, Nielson et al. [16] increased the pH value of the reaction mixture and demonstrated that butyric acid was not adsorbed on to bonopore; however, it is not clear whether this approach would be applicable to all the adsorbents and acetic acid.

As a result of these studies, it appears that adsorption and recovery of butanol/ABE from model solutions and fermentation broth is more economical than other techniques such as distillation, pervaporation, gas-stripping and liquid–liquid extraction. Such an energy-efficient recovery of butanol is expected to revive an interest in the commercial production of butanol from

renewable resources or agricultural biomass. The general characteristics of an adsorbent should include quick adsorption, high adsorption capacity, low cost, and ease of desorption and regeneration. The data that are available in the literature on the adsorption of butanol have been presented as outlined in the objective of this manuscript.

Conclusions

Three efficient adsorbents have been reported for separation of butanol from aqueous solutions or fermentation broth, namely silicalite, bone charcoal/charcoal, and polyvinylpyridine. Use of silicalite appears to be more attractive, as it can be used to concentrate butanol from dilute solutions, 5–810 g L⁻¹, and results in complete desorption. Further, silicalite can be regenerated by heat treatment. The energy requirement for butanol recovery by the adsorption–desorption process has been calculated to be 1,948 kcal kg⁻¹ butanol as compared to 5,789 kcal kg⁻¹ butanol by steam-stripping distillation. Other techniques such as gas-stripping and pervaporation require 5,220 and 3,295 kcal kg⁻¹ butanol, respectively. Use of bone charcoal or activated charcoal resulted in adsorption of butanol at the rate of 206–252 mg g⁻¹ of the adsorbent, however, desorption was incomplete. Successful application of polyvinylpyridine has been reported to recover ABE from fermentation broth. The concentration of butanol in the displacer phase (methanol) was reported to be rather low at 30–40 g L⁻¹ which would require further distillation. Fermentation parameters, however, were reported to have improved significantly. It is suggested that silicalite be used in butanol fermentations to improve fermentation parameters in addition to its already proven energy-efficient recovery.

Acknowledgements N. Qureshi would like to thank Holly Brining and Mark Maroon for their contribution to this manuscript.

References

1. Maddox IS (1989) The acetone-butanol-ethanol fermentation: recent progress in technology. *Biotechnol Genet Eng Rev* 7:189–220
2. Ladisch MR (1991) Fermentation-derived butanol and scenarios for its uses in energy-related applications. *Enz Microbial Technol* 13:280–283
3. Ezeji TC, Qureshi N, Blaschek HP (2004) Acetone butanol ethanol (ABE) production from concentrated substrate: reduction in substrate inhibition by fed-batch technique and product inhibition by gas stripping. *Appl Microbiol Biotechnol* 63:653–658
4. Qureshi N, Blaschek HP (2001) Evaluation of recent advances in butanol fermentation, upstream, and downstream processing. *Bioprocess Biosystems Eng* 24:219–226
5. Friedl A, Qureshi N, Maddox IS (1991) Continuous acetone-butanol-ethanol (ABE) fermentation using immobilized cells of *Clostridium acetobutylicum* in a packed bed reactor and integration with product removal by pervaporation. *Biotechnol Bioeng* 38:518–527

6. Qureshi N, Maddox IS, Friedl A (1992) Application of continuous substrate feeding to the ABE fermentation: Relief of product inhibition using extraction, perstraction, stripping and pervaporation. *Biotechnol Prog* 8:382–390
7. Qureshi N, Meagher MM, Huang J, Hutkins RW (2001) Acetone butanol ethanol (ABE) recovery by pervaporation using silicalite-silicone composite membrane from fed-batch reactor of *Clostridium acetobutylicum*. *J Memb Sci* 187:93–102
8. Groot WJ, van der Lans RGJM, Luyben KChAM (1992) Technologies for butanol recovery integrated with fermentations. *Process Biochem* 27:61–75
9. Qureshi N, Dien B, Saha BC, Ezeji TC, Blaschek HP, Cotta MA (2003) Separation of butanol from fermentation broth by pervaporation: mass flux and energy balance. In: Paper presented at the Annual Meeting of American Institute of Chemical Engineers (AIChE), San Francisco, CA, 162
10. Qureshi N, Cotta MA (2004) Energy requirement for butanol recovery from fermentation broth using adsorption as an alternative technique. In: Proceedings of 26th symposium on biotechnology for fuels and chemicals, Chattanooga, TN, p 116
11. Milestone NB, Bibby DM (1981) Concentration of alcohols by adsorption on silicalite. *J Chem Technol Biotechnol* 31:732–736
12. Das K, Soni BK, Chose, TK (1987) Static and column studies on selective adsorption-desorption of butanol. In: Proceedings 4th European congress on biotechnol 1:76–78
13. Meagher MM, Qureshi N, Hutkins RW (1998) Silicalite membrane and method for the selective recovery and concentration of acetone and butanol from model ABE solutions and fermentation broth. U.S. Patent 5,755,967
14. Groot WJ, Luyben KChAM (1986) In situ product recovery by adsorption in the butanol/isopropanol batch fermentation. *Appl Microbiol Biotechnol* 25:29–31
15. Nielsen L, Larsson M, Holst O, Mattiasson B (1987) Polymers as adsorbents for extractive bioconversions applied to the ABE-fermentation. In: Proceedings 4th European congress on biotechnol 2:293
16. Nielsen L, Larsson M, Holst O, Mattiasson B (1988) Adsorbents for extractive bioconversion applied to the acetone-butanol fermentation. *Appl Microbiol Biotechnol* 28:335–339
17. Yang X, Tsai G-J, Tsao GT (1994) Enhancement of in situ adsorption on the acetone-butanol fermentation by *Clostridium acetobutylicum*. *Separation Technol* 4:81–92
18. Maddox IS (1982) Use of silicalite for the adsorption of n-butanol from fermentation liquors. *Biotechnol Lett* 4:759–760
19. Ennis BM, Qureshi N, Maddox, IS (1987) In-line toxic product removal during solvent production by continuous fermentation using immobilized *Clostridium acetobutylicum*. *Enzyme Microbial Technol* 9:672–675
20. Yang X, Tsao GT (1995) Enhanced acetone-butanol fermentation using repeated fed-batch operation coupled with cell recycle by membrane and simultaneous removal of inhibitory products by adsorption. *Biotechnol Bioeng* 47:444–450
21. Holtzapple MT, Brown RF (1994) Conceptual design for a process to recover volatile solutes from aqueous solutions using silicalite. *Separat Technol* 4:213–229